



# CsF and alumina: A mixed homogeneous–heterogeneous catalytic system for the transesterification of sunflower oil with methanol

J. Ni <sup>a,b</sup>, D. Rooney <sup>a</sup>, F.C. Meunier <sup>a,b,\*</sup>

<sup>a</sup> CentACat, School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland, United Kingdom

<sup>b</sup> Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 Bd Maréchal Juin, 14050 Caen, France

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## ABSTRACT

The activity and nature (i.e. heterogeneous and/or homogeneous) of catalysts based on CsF supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> were investigated for the transesterification of vegetable oil with methanol. The effect of the activation temperature, CsF loading and the reusability in a recirculating reactor were first studied. CsF/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> exhibited the highest activity for a CsF loading of 0.6 mmol/g and when activated at 120 °C. An important aspect of this study is the effect of CsF leaching into the reaction mixture, which is attributed to the high solubility of CsF in methanol, leading to a complete loss of activity after one run. It was identified that the activity of the catalyst resulted from a synergy between alumina and dissolved CsF, the presence of both compounds being absolutely necessary to observe any conversion. The use of an alumina with a higher surface area resulted in a far greater reaction rate, showing that the concentration of surface site on the oxide (probably surface hydroxyl) was rate-limiting in the case of the experiments using the low surface area  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. This work emphasizes that combined homogeneous–heterogeneous catalytic systems made from the blending of the respective catalysts can be used to obtain high conversion of vegetable oil to biodiesel. Despite the homogeneous/heterogeneous dual character, such a catalytic system may prove valuable in developing a simple and cost-effective continuous catalytic process for biodiesel production.

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## 1. Introduction

The use of heterogeneous catalysts in the transesterification of vegetable oils into biodiesel has been widely investigated [1–7] due to its merits such as easier separation of products and catalysts after reaction [8], no formation of soaps through free fatty acid neutralization by NaOH or triglyceride saponification, and high reaction yield (>95%) in systems with high molecular weight alcohols [9]. Among catalytic solids, supported fluorides exhibit a basicity higher than that of MgO, CaO or hydrotalcites [10] and have demonstrated high catalytic activities in a wide range of typically base-assisted reactions [11–13]. Fluorides in transesterification reactions increase the nucleophilicity of oxygen in alcohol molecules through strong hydrogen bonding [14] and also activate carbonyl groups in triglycerides [15], facilitating reaction completion.

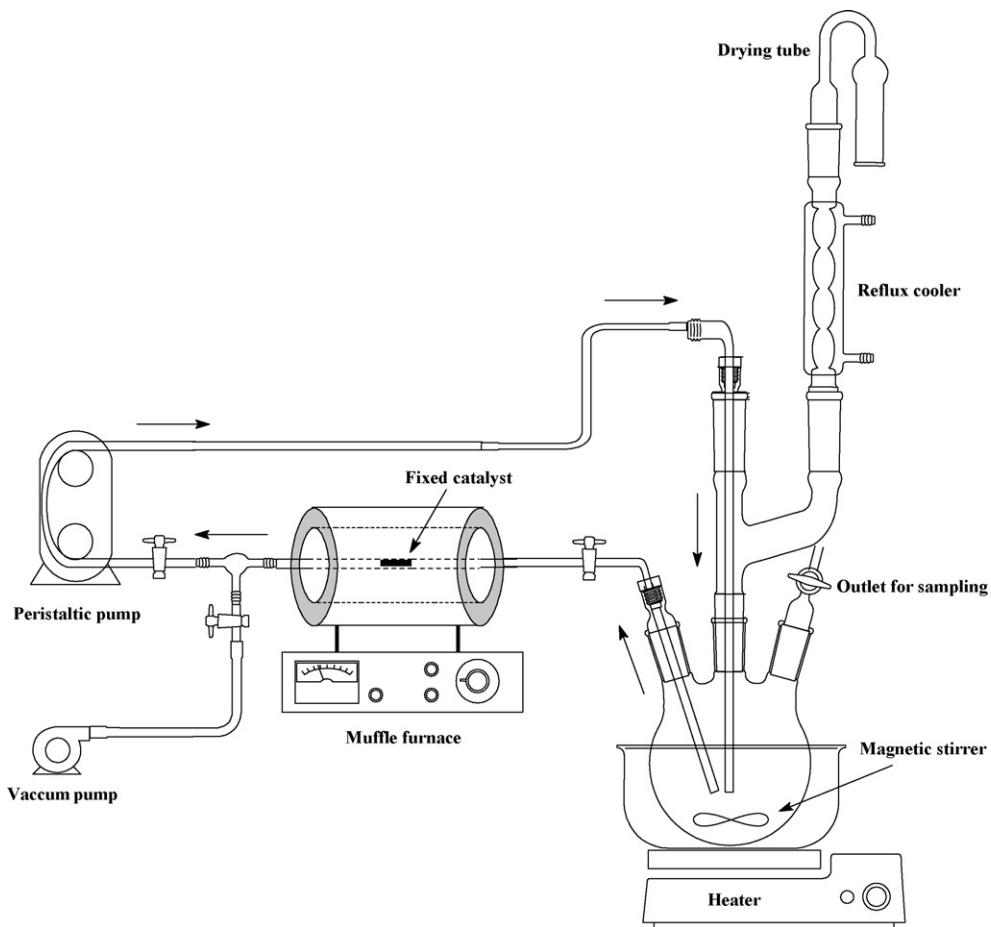
However, the interaction between fluoride and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> leads to fluoride compounds with a lower basicity than that of the parent alkaline fluoride precursor [10], thus higher loadings of fluorides

can be necessary to compensate the basicity loss. These observations motivate the synthesis and utilisation of fluorides supported on a less reactive support, in particular  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Clacens et al. [16] have reported the benefit of using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> instead of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a support for CsF for base-catalysed reactions such as the Michael addition of cyclohexene-2-one with nitroalkanes and in the synthesis of alkyl carbonates. Despite the much lower surface area of the catalyst based on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the CsF/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> displayed far superior catalytic activity [16]. These authors also stressed the low activation temperature required (merely 120 °C) to activate the CsF/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

Interestingly, no work on the use of CsF/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has yet been reported for the transesterification of vegetable oils with methanol into biodiesel (i.e. fatty acid methyl ester, FAME). A high surface area mesostructured alumina was used in the case of the work carried out by Verziu et al. [10]. The CsF/alumina samples were also calcined at high temperature (i.e. 400 °C), which resulted in the formation of mixed compounds of CsF and alumina [10]. The effect of the activation temperature is here investigated using CsF supported over a commercial  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The possible role of CsF dissolution in the reaction mixture is also to be clarified, since fluorine leaching is sometimes reported [10] and that unsupported CsF is known to lead to active species [16]. The results obtained here will show that the most practical application of this catalytic system could rather be based on a process combining homogeneous (i.e. CsF dissolved in methanol) and heterogeneous (i.e. alumina) moieties.

\* Corresponding author at: Laboratoire Catalyse et Spectrochimie, CNRS, Université de Caen, ENSICAEN, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France. Tel.: +33 0231452731; fax: +33 0231452822.

E-mail address: [frederic.meunier@ensicaen.fr](mailto:frederic.meunier@ensicaen.fr) (F.C. Meunier).



**Fig. 1.** Schematic layout of the reactor system used for the experiments involving the recirculation of the reaction mixture through a fixed catalytic bed.

## 2. Experimental

### 2.1. Catalyst and reagents

Commercial caesium fluoride (99.99%) from Aldrich and  $\alpha$ -alumina (99.9% purity,  $5.48 \text{ m}^2/\text{g}$ ) from Alfa Aesar were used as precursor for preparation of  $\alpha$ -alumina-supported fluorides. The  $\gamma$ -alumina sample was obtained from BDH ( $26.0 \text{ m}^2/\text{g}$ ). The commercial grade sunflower oil was bought at Tesco supermarkets (density 0.91, fat composition: saturated 12.0 wt.%, mono-unsaturated 23.0 wt.%, polyunsaturates 65.0 wt.%, free fatty acid (FFA) content: 0.088 wt.%). The methanol (MeOH) (99.8% for HPLC) was purchased from VWR.

The catalyst, CsF supported on  $\alpha$ - $\text{Al}_2\text{O}_3$ , was prepared by an impregnation method using aqueous solutions of known concentrations of CsF as reported elsewhere [17]. The required amount of alumina was placed into a given quantity of deionised water containing the appropriate amount of CsF. Water was evaporated at  $80^\circ\text{C}$  and the solid was then air-dried at  $120^\circ\text{C}$  overnight. Prior to the catalytic tests, the catalysts were evacuated under  $10^{-3} \text{ Pa}$  at  $120^\circ\text{C}$  for 6 h, unless otherwise stated.

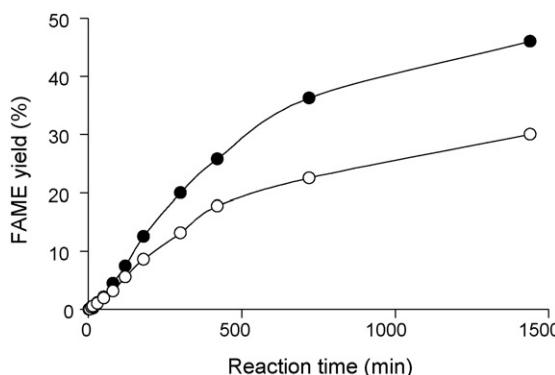
### 2.2. Catalytic experiments

30 ml of sunflower oil and the desired amount of methanol were placed into a stirred round bottom flask of  $100 \text{ cm}^3$  volume fitted with a reflux condenser using a steady flow of water passing through to avoid methanol loss. The flask was immersed in an oil bath with a thermocouple to keep the bath temperature at  $70^\circ\text{C}$  constantly throughout the reaction. The resulting flask tempera-

ture was monitored by an thermocouple plunging into the reaction mixture and remained at  $65 \pm 1^\circ\text{C}$ .

Two types of experiments were carried out, one of which was a simple batch reaction, for which a known mass of catalyst was simply added to the round bottom flask containing the reaction mixture and stirred at 1000 rpm. In the second type of experiments, the catalyst was placed in a quartz plug-flow tube reactor between a quartz filter and one layer of quartz wool (Fig. 1). The reaction mixture was stirred at the speed of 1000 rpm before being pumped into the quartz plug-flow tube using a peristaltic pump. The second mode, based on a fixed bed, was more appropriate to assess the catalyst reusability, by preventing any catalyst loss during the separation of the reaction products. In both cases 1 g of catalyst was used. The reaction medium was not a homogeneous solution, as it clearly separated into two phases (one alcohol-rich and one oil-rich) when the stirring was stopped.

For both reaction types, the catalyst was dried at  $120^\circ\text{C}$  (unless otherwise stated) under vacuum for 6 h prior to the transesterification reaction before being contacted with the reaction mixture. The fresh catalyst was covered by the reactants, preventing exposure to water and  $\text{CO}_2$ . During the transesterification reaction, 50  $\mu\text{l}$  of samples were drawn from one outlet of flask using a 1 ml syringe at certain intervals, then introduced immediately into sample bottles containing pre-weighed 5  $\mu\text{l}$  of methyl pentadecanoate as an internal standard plus 20  $\mu\text{l}$  of MSTFA (CAS no.: 24589-78-4) as derivatisation reagent. The weight of sample was obtained by comparing the weight of sample bottle before adding the samples and that afterwards. Then 80  $\mu\text{l}$  of hexane was introduced into sample bottle as solvent. The samples were subjected to the GC analysis. The results are presented in the form of the FAME yield, which



**Fig. 2.** Comparison of the catalytic activity of the CsF/α-Al<sub>2</sub>O<sub>3</sub> (0.6 mmol/g) prepared with (○) calcined α-Al<sub>2</sub>O<sub>3</sub> and (●) α-Al<sub>2</sub>O<sub>3</sub> as received.

corresponds to the ratio between the number of moles of methyl ester formed and that of triglycerides initially present. The number of moles of triglycerides present in our sunflower oil was calculated using the typical molecular weight of sunflower oils, i.e. 879.5 g/mol.

Some batch-mode experiments were made by placing first the activated alumina into the reaction mixture in the round bottom flask. The CsF was dissolved in methanol at ambient temperature under an inert atmosphere. The CsF methanol solution was then injected with a syringe directly into the reaction flask at the reaction temperature.

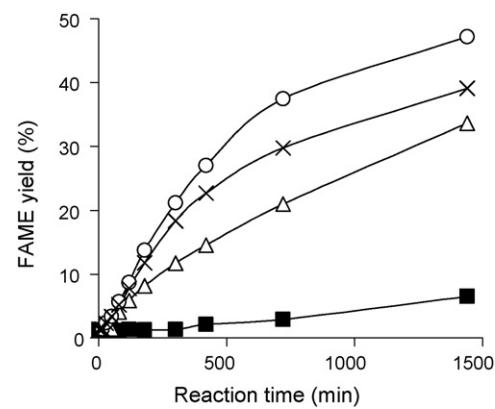
### 2.3. Sample characterization

The sample Cs content was measured by atomic absorption spectroscopy (AAS) carried out over a spectrophotometer. Only the Cs content of the sample was measured. The XRD patterns were recorded in an in situ cell under flowing N<sub>2</sub> on a PANalytical X'Pert Pro MPD diffractometer equipped with an Anton Paar XRK 900 reaction chamber. A parallel detection system (X'Celerator detector from PANalytical) with a diffracted beam monochromator was used in continuous scanning mode from 10° to 70° (2θ) (127 channels of 0.0167° (2θ), 4.7 s/step, i.e. 600 s/data point). The X-ray source contained was a copper cathode and the CuK $\alpha$ , wavelength 1.5405 Å was used. The phases were identified using the power diffraction file (PDF) database (JCPDS, International Centre for Diffraction Data).

## 3. Results and discussion

### 3.1. Effect of a pre-treatment of the α-Al<sub>2</sub>O<sub>3</sub> prior to CsF deposition

The α-Al<sub>2</sub>O<sub>3</sub> used was a commercial material (i.e. not produced in-house), therefore its surface may have been re-hydrated with time since it was manufactured. Therefore, the concentration of OH- group on the surface was expected to be modified following a calcination, even if carried out at a temperature lower than that of the manufacturing process. The catalytic activity of powdered CsF/α-Al<sub>2</sub>O<sub>3</sub> prepared with either α-Al<sub>2</sub>O<sub>3</sub> as received or the same oxide calcined by us at 1000 °C were compared. The CsF/α-Al<sub>2</sub>O<sub>3</sub> powder prepared with the as received α-Al<sub>2</sub>O<sub>3</sub> exhibited a somewhat higher activity than that prepared with the calcined α-Al<sub>2</sub>O<sub>3</sub> (Fig. 2). It has been proposed that, for supported fluorides, the catalytic reactions occur largely at the surface of the alumina involving physisorbed fluoride ions interacting with surface hydroxyl groups [18]. A better dispersion of the fluoride over the surface of the support would result in enhanced reagent reactivity. As the surface areas of the catalysts were essentially identical (5.04 m<sup>2</sup>/g for the



**Fig. 3.** Comparison of the activity of CsF/α-Al<sub>2</sub>O<sub>3</sub> (0.6 mmol/g) activated at different temperatures: (x) 80 °C, (○) 120 °C, (Δ) 160 °C and (■) 200 °C.

calcined material and 5.48 m<sup>2</sup>/g for the fresh catalyst), the activity loss observed upon calcination could possibly be related to a decrease in the concentration of Al–OH species on catalyst surface.

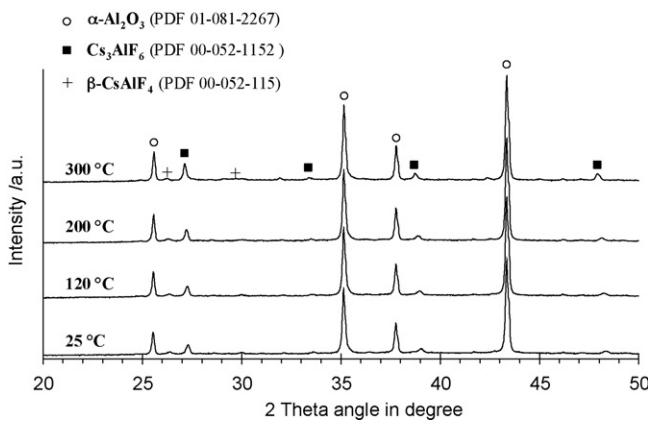
### 3.2. Effect of the pre-treatment of CsF/α-Al<sub>2</sub>O<sub>3</sub> prior to the reaction

The water content of fluoride reagents was reported to be a critical factor in determining the reactivity of these compounds [17]. Since the nature of CsF is highly hygroscopic, it is necessary to remove adsorbed water by drying the CsF/α-Al<sub>2</sub>O<sub>3</sub> prior to any transesterification reaction. In this work batch reactions were carried out with CsF/α-Al<sub>2</sub>O<sub>3</sub> powder activated (i.e. vacuum-dried) at 60, 120, 160 and 200 °C, respectively. The maximum of activity was obtained with the sample dried at 120 °C (Fig. 3). Alongside water, adsorbed carbon dioxide (from ambient air) could also be a poison to the catalyst basic sites. The main reason for the observed increase of activity upon activation at 120 °C is therefore likely to be both the removal of weakly sorbed water and CO<sub>2</sub> from the sample surface. It must be noted that Figueras et al. [16] reported that 120 °C was also a sufficient activation temperature for the base-catalysed reaction studied by these authors over a similar sample.

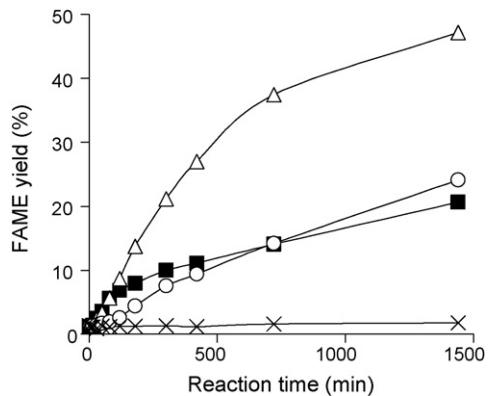
It must be stressed that the activation at 200 °C resulted in a very low activity. The catalyst activated at 200 °C turned grey (from white) and formed dark agglomerates under vacuum, suggesting that the loss of activity was due to the destruction of active species at this temperature. This result is consistent with those reported earlier for KF-based samples that high drying temperatures result in significant structural damage to the reagents with resulting loss in activity [17].

A temperature-programmed XRD analysis was carried out to investigate the presence of bulk crystalline phases, in particular at the low temperatures of interest to this work (Fig. 4). Apart from the peaks associated with α-Al<sub>2</sub>O<sub>3</sub>, Cs<sub>3</sub>AlF<sub>6</sub> and β-CsAlF<sub>4</sub> phases were observed already at room temperature and up to 300 °C. There were other minor peaks, which could not be unequivocally identified. Note that no CsF peaks were observed. As in the case of the α-Al<sub>2</sub>O<sub>3</sub>-supported KF and CsF materials reported by Figueras et al. [16,19], it is likely that a major fraction of the CsF was present as an amorphous phase on our catalyst. Other phases richer in Cs might have been present such as Cs<sub>2</sub>O, CsOH or Cs<sub>2</sub>CO<sub>3</sub>, also those were not detected by XRD.

The loss of activity observed for activation temperatures above 200 °C could be due to a modification of the structure of the catalyst. A fraction of the amorphous CsF could (i) sinter and/or (ii) be converted in other F-containing phases (amorphous or crystalline). In the case of a similar catalyst, i.e. KF supported on α-Al<sub>2</sub>O<sub>3</sub>, Figueras



**Fig. 4.** In situ XRD patterns of CsF/α-alumina at 25, 120, 200 and 300 °C under flowing N<sub>2</sub>.



**Fig. 5.** Activity of CsF/α-Al<sub>2</sub>O<sub>3</sub> with various loadings of CsF: (x) 0.3 mmol/g, (○) 0.5 mmol/g, (△) 0.6 mmol/g and (■) 0.7 mmol/g.

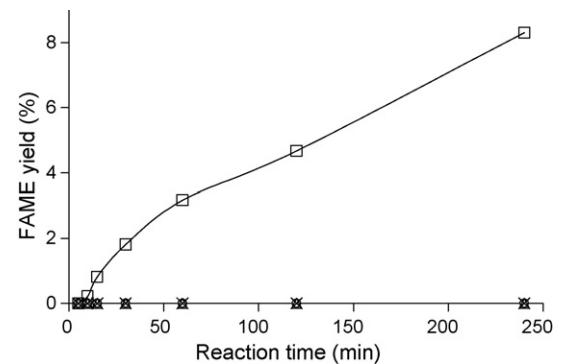
and co-workers [19] reported evidence of solid-state reaction of KF with the support, which led to various inactive (or less active) phases such as K<sub>3</sub>AlF<sub>6</sub>, K<sub>2</sub>AlF<sub>5</sub> and KAlO<sub>2</sub>. It can therefore be safely suggested that the major loss of activity observed for activation above 120 °C was due to the agglomeration of CsF (still remaining amorphous) and the formation of less reactive phases.

### 3.3. Catalytic activity of powdered CsF/α-Al<sub>2</sub>O<sub>3</sub> with various CsF loadings

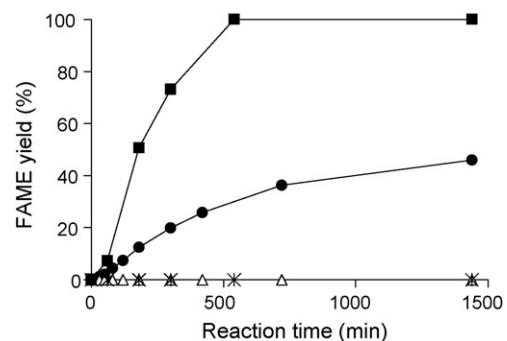
The CsF/α-Al<sub>2</sub>O<sub>3</sub> samples were prepared with various loadings of CsF over the support, namely 0.3, 0.5, 0.6 and 0.7 mmol/g. The catalyst with a loading of 0.6 mmol/g displayed the highest activity compared with the other catalysts, while the catalyst with a loading of 0.3 mmol/g seemed not to have any activity in the transesterification reaction (Fig. 5). (Note: A loading of 0.6 mmol/g of CsF theoretically corresponds to about 8.0 wt.% of caesium and 1.1 wt.% of fluorine in the sample.) The loss of activity observed above 0.6 mmol/g was possibly due to (i) CsF aggregation, thus reducing the dispersion of CsF on the α-Al<sub>2</sub>O<sub>3</sub> support and/or (ii) a too low concentration of surface hydroxyls (as it was shown above that part of the alumina chemically reacted with the salt, Fig. 4), which could be involved in the catalytic cycle (*vide infra*).

### 3.4. Reusability of CsF/α-Al<sub>2</sub>O<sub>3</sub>

The reusability of the CsF/α-Al<sub>2</sub>O<sub>3</sub> (loaded at 0.6 mmol/g) catalyst was examined over four consecutive runs (Fig. 6), each of 4 h in the recirculating system (see Fig. 1). Using a recirculation



**Fig. 6.** Activity of the CsF/α-Al<sub>2</sub>O<sub>3</sub> over several consecutive runs: (□) initial run, (Δ) second run, (○) third run and (×) fourth run.



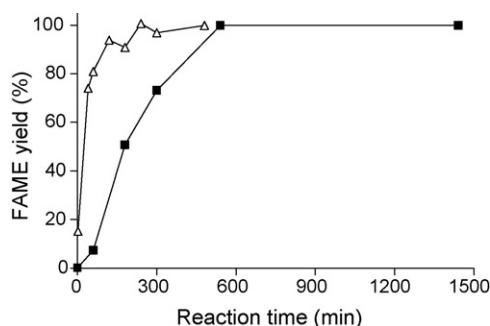
**Fig. 7.** Activity of (Δ) 0.6 mmol of bulk CsF, (×) 1 g of α-Al<sub>2</sub>O<sub>3</sub>, (●) 1 g of 0.6 mmol/g CsF/α-Al<sub>2</sub>O<sub>3</sub> and (■) a mixture of 0.6 mmol of CsF (initially dissolved in methanol) + 1 g α-Al<sub>2</sub>O<sub>3</sub> for the transesterification of vegetable oil.

system with a fixed catalyst bed allows monitoring catalyst deactivation more easily with consecutive cycles without any need to separate reaction mixture and catalyst between runs (thus avoiding catalyst particle loss during separation). The conversion was essentially increasing linearly with time, indicating that the reaction rate was constant for this first cycle. However, no catalytic activity was observed in any of the three subsequent runs. Further reactions using an extended reaction time of 24 h in both recirculating and batch system also showed no activity (data not shown).

The elemental analysis revealed that the Cs concentration had decreased from 7.36 wt. % down to 0.38 wt.% after use. In order to assess whether the leaching of CsF was caused by the methanol, we washed the CsF/α-Al<sub>2</sub>O<sub>3</sub> with 10 ml of anhydrous methanol twice prior to the reaction. For each washing, the mixture of methanol and catalyst was allowed to settle and separate, then the liquid was taken away and fresh methanol was added. The result showed that there was essentially no catalytic activity after methanol-washing. This observation suggests that leaching was taking place during the transesterification reaction, which was due to the solubilisation of CsF in the methanol-rich phase.

### 3.5. Nature of the active phase

The nature of the active phase was investigated by comparing the activity of the supported CsF catalysts (using 1 g of 0.6 mmol/g CsF/α-Al<sub>2</sub>O<sub>3</sub>) to that of (i) 0.6 mmol of bulk CsF pre-dissolved in MeOH, (ii) 1 g of α-Al<sub>2</sub>O<sub>3</sub> and (iii) a blending of 0.6 mmol of CsF (initially dissolved in methanol) + 1 g of α-Al<sub>2</sub>O<sub>3</sub> (Fig. 7). Using CsF alone or α-Al<sub>2</sub>O<sub>3</sub> alone resulted in no observable catalytic activity, showing that neither component could catalyse by itself the transesterification. Interestingly, the mixture of the separate constituents exhibited a threefold higher activity than that of the



**Fig. 8.** Activity of a mechanical mixture of 0.6 mmol of CsF (initially dissolved in methanol) added to 1 g of ( $\triangle$ )  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ( $\blacksquare$ )  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for the transesterification of vegetable oil into FAME.

CsF/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. This observation shows that:

1. There is a synergy between CsF and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> leading to an active phase active in triglyceride transesterification.
2. The ex situ deposition of CsF on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> does not reveal the full potential of the system. In other words, the deposition/calcination step inhibits the sample activity.
3. CsF, one of the active species (likely through the fluoride ion [11–15]) is most likely in solution (near to the surface site involved in the catalysis) rather than directly anchored onto the alumina surface.

This last point is supported by the fact that most of the CsF salt of the CsF/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst is readily leached into the methanol solution (see Section 3.4) and that CsF predeposition on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> wasted some of the fluoride by attaching it too strongly to the surface, as the highest activity was observed for the blended mixture (Fig. 7). Therefore, it would be unlikely that the most active operating state of the sample would consist of fluoride chemically bound to the surface.

### 3.6. Utilisation of a high surface $\gamma$ -alumina for the blending test

The activity of a blended mixture of CsF (dissolved in MeOH) and a  $\gamma$ -alumina presenting a surface area ( $26\text{ m}^2/\text{g}$ ) higher than that of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ( $5.04\text{ m}^2/\text{g}$ ) used in the previous sections was measured. The initial rate of reaction was markedly increased when using the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, as compared to the case of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Fig. 8). The initial productivity of methyl ester is reported in Table 1 for these catalysts and some materials previously reported in the literature, for which similar experimental conditions were used.

The FAME productivity appears to be similar or even higher in the case of the blend methanol-dissolved CsF and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (this work) as compared to the case of the CsF supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (from Ref. [10]). It was also reported by Verziu et al. [10] that alumina used by itself showed no catalytic activity. These observations are similar to those obtained for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-based materials (see previous section).

### 3.7. Discussion

The present work has unveiled some aspects of the catalytic activity of CsF and alumina-based systems for the transesterification of sunflower oil with methanol. The most interesting observation is that it is not necessary to prepare a conventional supported CsF on alumina (generally involving high calcination temperatures) to obtain an active catalyst. The mere blending of CsF dissolved in methanol and alumina directly inside the reactor at the reaction temperature of 65 °C is sufficient to obtain an active catalytic system (Fig. 7). It cannot be totally excluded that an

alumina–CsF mixed solid would be formed in situ and would be the only or main active catalytic species. However, our work stress that it is not necessary to prepare a strongly bound fluoride sample (i.e. through impregnation and high temperature calcination) to obtain an active formulation, but that both compounds act in a synergistic manner to form an active system simply by contacting those at in the reaction medium at reaction temperature of 65 °C.

Essayem and co-workers [20] recently reported the outstanding transesterification activity of Cs-modified ZrO<sub>2</sub>. The Cs was deposited by ionic-exchange followed by high temperature calcination (i.e. 550 °C) and washing in ethanol to remove weakly bound Cs species. It is unlikely that a similar active species was present on our sample, because the CsF methanol solution and the alumina were only contacted at the reaction temperature of 65 °C at the most in the case of the data reported in Fig. 8.

The possible formation of caesium hydroxide, which would be highly soluble in the methanol phase, cannot be totally excluded [21]. Such basic compounds could then be responsible for part of the activity. Figueras and co-workers [19] actually reported the formation of potassium hydrogenocarbonate over KF supported on  $\alpha$ -alumina, probably deriving from the carbonation of KOH. It must be stressed that these authors still assigned the basic nature of the catalytic properties (assessed via the Michael condensation of 2-cyclohexen-1-one with nitroalkanes) to the alumina-supported KF. More work would be needed to determine whether the formation of Cs(OH)<sub>2</sub> would be significant in our case and its possible impact on the activity.

Our work actually strongly suggests that CsF leached from the catalyst is a crucial element of the catalytic activity and therefore that many formulations based on similar materials may involve homogeneous catalysis, at least in part. The leaching will of course depends significantly on the polarity of the reaction medium used. In the case of the synthesis of unsymmetrical organic carbonates from diols, Figueras and co-workers [22] showed that their CsF/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was recyclable, although some deactivation was observed with each cycles. The authors showed that CsF leaching was not significant in these conditions and proposed that catalyst loss and/or water poisoning was the likely cause of the loss of activity.

The fact that the calcination temperature of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> affects the activity (Fig. 2), while the sample surface area is essentially unchanged, suggests that the surface hydroxyl groups matter more than the nature of the cation (e.g. Al<sup>3+</sup>) present in the oxide. This view is further supported by the fact that the higher activity observed (see Table 1) in the case of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (i.e.  $34\text{ ml h}^{-1}\text{ g}^{-1}$ ) as compared to that measured in the case of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (i.e.  $2.5\text{ ml h}^{-1}\text{ g}^{-1}$ ) is not algebraically related to the increase of the alumina surface areas (from 5.48 to 26.0). It would be useful to determine the concentration of surface hydroxyl groups, although this may not be straightforward and not all surface hydroxyl groups may exhibit the same catalytic activity.

It must be emphasised again that the use of CsF alone or alumina alone does not lead to any detectable activity. Similar observations were obtained by Baba et al. [17] in a study of the metathesis of silylalkynes and cross-metathesis of silylalkyne and 1-alkyne. These authors found that Al<sub>2</sub>O<sub>3</sub> and KF heated at 200 °C under vacuum, showed no catalytic activity when used separately, while the simultaneous presence of KF and alumina led to an active system. More, KF supported on SiO<sub>2</sub>, TiO<sub>2</sub>, and activated carbon showed no catalytic activity, suggesting that not all supports may be suitable. Appropriate surface hydroxyl concentration and base strength may be required.

In the case of the present study regarding CsF and aluminas ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) for vegetable oil transesterification, the exact nature of the active site and character of the reaction (i.e. partly homogeneous or fully heterogeneous) is still uncertain and more

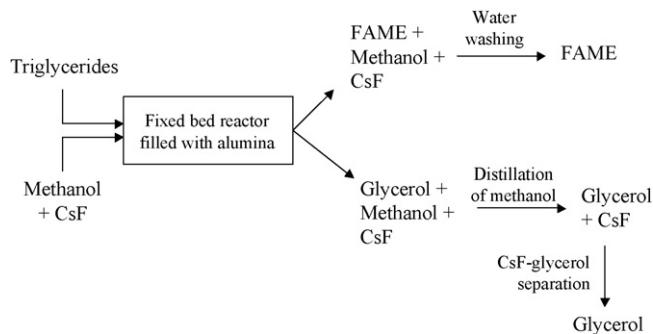
**Table 1**

Productivity of FAME on various catalytic systems used for vegetable oil transesterification with methanol at 65 °C (calculated for vegetable oil conversions up to between 20 and 75%, using the slope of the average initial line giving conversion versus time). The three first entries are from this work.

Samples	CsF supported on $\alpha\text{-Al}_2\text{O}_3$	CsF/MeOH blended with $\alpha\text{-Al}_2\text{O}_3$	CsF/MeOH blended with $\gamma\text{-Al}_2\text{O}_3$	CsF supported on $\gamma\text{-Al}_2\text{O}_3^a$	CaO <sup>b</sup>
FAME productivity (ml h <sup>-1</sup> g <sup>-1</sup> )	1.1	2.5	34	28	420

<sup>a</sup> From Ref. [10], measured at 75 °C. A 20 wt.% CsF/ $\gamma\text{-Al}_2\text{O}_3$  was used, the  $\gamma\text{-Al}_2\text{O}_3$  exhibiting a surface area of 280 m<sup>2</sup>/g.

<sup>b</sup> From Ref. [27], measured at 60 °C.



**Fig. 9.** Schematic representation of a biodiesel continuous production process based on the alumina–CsF catalytic system. The alumina is located in a fixed bed reactor through which is passed the feedstock (vegetable oil or recycled oil) and the methanol, which also contains dissolved CsF. The salt, which does not lead to any water or soap formation, and the methanol can be recovered from reactor products and recycled.

work in needed to clarify these points. For the same reaction catalysed by CaO, it was recently shown that both homogeneous and heterogeneous pathways could be active and that the corresponding predominance of either pathway depended on the experimental conditions [27]. CaO systems appeared to be much more active than the formulations reported here (Table 1), but CaO solubilise more significantly in the presence of glycerol, the main reaction product alongside FAME, by forming calcium diglyceroxide [27]. The formation of Ca colloidal particles under similar experimental conditions was also recently reported [23], which may then lead to scum formation and reactor blockage.

Such detrimental occurrences are unlikely in the case of a system based on alumina and methanol-dissolved CsF. On the one hand, alumina is totally insoluble in methanol, glycerol or in the non-polar phases, i.e. vegetable oil and FAME. On the other hand, CsF is readily dissolved in hot methanol (the solubility of CsF is 1.91 g per g of methanol at 18 °C) and glycerol. The salt can be recovered after reaction from the alcoholic phase made of glycerol and unreacted methanol most efficiently by first distilling off the methanol and then by separating CsF from glycerol, which can be achieved via several methods [24]. One of the glycerol–salt separation methods is based on chromatographic separation techniques using high-performance chromatographic separation resin [25]. Salts are poorly soluble in vegetable oil and FAME and any CsF present in the biodiesel produced will be easily recovered during the water-washing step required to obtain alcohol-free biodiesel. Therefore a simple biodiesel production process could comprise a fixed bed made of alumina particles and CsF continuously injected with the methanol (Fig. 9).

The effect of trace amounts of free fatty acid (FFA) and water should yet be assessed. Contrary to the bases KOH or NaOH used in purely homogeneous system, the CsF salt does not react with the FFA to form water and therefore should dramatically reduce the formation of emulsion and foaming during biodiesel production. The formation of any significant concentration of HF is not expected, because of the typical low concentration of FFA in oils and the low acidity of FFA ( $pK_a > 4$ ) as compared to that of HF ( $pK_a = 3.1$ ).

It must be stressed that we herein did not attempt to determine the optimal proportion of CsF and alumina (or its optimal surface area or/and surface hydroxyl concentration), neither the nature of the best salt and oxide to be used. It is likely that many other combinations of salt and oxide may lead to better catalytic activities. The object of the present contribution was merely to unravel some aspects of the catalysis associated with supported CsF catalysts and eventually also led to this new concept of dual homogeneous/heterogeneous catalytic system. It would probably be more appropriate to determine first the most active combination of oxide and fluoride salt (as well as the optimum ratio between oxide and salt) before exploring in some depth the associated reaction mechanism(s) and the nature of the active species.

In fact, Sun et al. [26] observed the complete deactivation of a KF/Eu<sub>2</sub>O<sub>3</sub> catalyst used for the transesterification of rapeseed oil with methanol after the first recycling, but the activity of the catalyst could be recovered by adding KF in the reaction system. However, the authors did not attempt to directly start with a mechanical mixture or blending of the salt and the plain oxide. The work of Sun et al. [26] yet supports our view that many other oxides may be used in place of alumina. Since alumina is a cheap, widely available and durable solid, any other material would have to lead to a significantly more active catalytic system (in combination with CsF or another salt) to be of greater interest.

#### 4. Conclusions

The transesterification of sunflower oil with methanol was studied using CsF and  $\alpha\text{-Al}_2\text{O}_3$ -based formulations. Sample optimisation in terms of CsF loading and calcination temperature were determined. An important leaching of Cs occurred during the first use, probably due to the solubility of CsF in methanol. It is suggested that for the present formulations (calcined at low temperatures) and using polar alcohol (methanol) the active site resulted from a synergy between alumina and solubilised CsF, both compounds being necessary to obtain a measurable activity. A catalytic system based on the blending of the  $\alpha\text{-Al}_2\text{O}_3$  and the CsF dissolved in methanol resulted in a catalytic system with a greater activity than the CsF supported on  $\alpha\text{-Al}_2\text{O}_3$ . More, the use of a high surface area  $\gamma\text{-Al}_2\text{O}_3$  resulted in an even higher activity. This work emphasizes that mixed homogeneous–heterogeneous catalytic systems made from simple blending of compounds can be used to obtain high conversion of vegetable oil to biodiesel. More work is needed to determine the optimum system (salt, oxide, and reaction conditions) and the corresponding reaction mechanism(s).

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